Attachment 1   **05/18/2018**   **Liqiang Wei**

I want to make a complaint that Ronald Hoffmann, et al have stolen, damaged, and oppressed my researches and research achievements on quantum interaction and energy scale principle and their applications, that especially include my creation of physical nature of chemical bonds and my creation of general electronic structure theories at various stages. I state the related story as follows.

In September 1998, I communicated to Roald Hoffmann regarding my idea or proposal on general quantum mechanical perturbation theory for both the qualitative understanding of all the chemical bonds and also the quantitative investigation of all the electronic structures for molecules and solids at various stages. Nevertheless, this idea or proposal of mine and the resulting one application have been robbed or stolen by him and his cooperators, that are now shown in the paper published in the year of 2000 cited as: Int. J. Quant. Chem. 77, 408-420 (2000). See Attachment 2 for this paper. Enclosed with this Attachment is also the copy of the envelop for the letter that Roald Hoffmann responded to my inquiry at that time for a possible postdoc position, that is, however, under the persecution and oppression as must be known. I have kept my original letter stating my proposal to him, that, nevertheless, has been altered or rephrased by someone unknown or Roald Hoffmann himself. It speaks the same idea or proposal as I have originally spoken but in the different way that even does not have the flattery that I originally gave to him within the letter. In addition to this alternation or rephrasing, my original handwriting displayed in my original letter for several corrections has also been varied as have been done for my many other documents or cases. I have therefore decided that it is better at the moment not to demonstrate the letter to the Court. Directly relevantly, a chapter drafted in the early of 1998 and initially for my thesis mentioned in another occasion that has the detailed presentation of my idea or proposal stated and the resulting applications that includes physical nature of chemical bonds has also some changes. For the paper being discussed that is by Ronald Hoffmann et al, in addition to the stated fact that it is steal or robbery, it has also been altered for two or three times or has three or four "versions" as I have seen it, that can only have one version legally, however![1] This further fraud that is falsification can be readily confirmed technically! Around 2003 or 2004, and at

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[1] As I have stated in another complaint too with case #: 18-cv-02095, any correction to a
paper that has been published can only be made via erratum or corrigendum.

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Abington, MA, I first noticed that the theft of my idea stated as similarly expressed in one sentence of their paper had been disappeared or removed from their paper, most probably their seeing my submission of my article [1] in 2001 that has shadowed their paper for its very low quality. This should be the second "version" of their paper. See Attachment 3 for my article [1]. Just one month ago that is on 03/29/2018, I have decided to have a lawsuit against Roald Hoffmann and have examined all the steals from his website for his publication list, and even cannot see this paper in his publication list for the year known. This should be the third "version" of their paper. At that time, I thought that he had withdrawn this paper sometime, seeing my article [2] or its most recent submission that can be seen as Attachment 2b in my other complaints with case #s: 18-cv-02082 or 18-cv-02088.[2] Two weeks ago that is on 05/04/2018, I have examined his website again for the publication list, but have surprisingly seen this paper again, and also its content has been altered dramatically or essentially as should be seen now. The alternation stated include the departure from the previous context of a semiempirical treatment and also an addition of study that is for degenerate situation that has not been seen in the earliest version of this paper. This is, nevertheless, the theft of my application of my general quantum mechanical perturbation theory to the address of energy eigenequation for single-particle states, that is my basis-set theory. The initial proposition of this basis set theory can be seen openly in my article [1], and its mathematical development has been stored in my personal computer and in my locked case in my private residency, that have been now both stolen by Roald Hoffmann et al.[3] However, it must be known that, except his Nobel Prize in Chemistry that is second to R. B. Woodward, Road Hoffmann is merely a computational quantum chemist. Also, his practicing of quantum chemical theories or methodologies is extremely limited that has been seen only for crude extended Huckel theory and urine DFT as known. As could be readily observed from all his publications, he has been devoid of a good aptitude or training in both of physics and mathematics. Even though he likes theory and has a great passion for the understanding

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[2] I also saw his paper on the theory of DFT cited as: J. Am. Chem. Soc., 121(14), 3414-3420 (1999) for the first time that is, I think, for the replacement of the presentation of this paper then.

[3] In the drafted chapter mentioned, I have also suggested a detailed construction of basis set that is based on hybrid atomic orbitals.

of chemical bonds and chemistry, he has been therefore still limited on this regard. There has been no any quantum physics and also there has been no any sense of quantum many-body theory that have been seen or expressed in all his publications until in recent years with the thefts of mine as being discussed or seen. Thereby, there has been no any basis and there has been no any ground at all for Ronald Hoffmann, together with his cooperators, to write this paper, that is steal or further falsification as being complained! For the most recent "version" of this paper that I have just looked upon, he and his coauthors have also falsified its citation that includes his earlier papers that must be false! Actually, upon refreshing my memory for a browsing of his publication list, the word "Perturbative" as shown in the title of this paper should be the first occurrence among all the titles of his publications, that is unfortunately steal or robbery!

A few years ago, I noticed that the citation list in my article [1] has been added by someone unknown or Roald Hoffmann himself to include a paper by him as now cited as the reference [4] there. For the reason described above, I have actually not cited this paper. There is another reason for my omission of this paper. It must be understood that the scheme of orbital interaction for the interpretation of chemical bonds that Roald Hoffmann has advocated and practiced within his school and in this paper has not been well known in chemistry community, and is actually another version of Walsh correlation diagram method adding orbital visualization. They both possess the same spirit and also both practice in the same scope, and both of them have been extremely limited as must be known and understood. Also, I want to tell that my development of the idea or proposal stated and the subsequent applications that includes physical nature of chemical bonds has nothing to do with this Walsh correlation diagram method and also this scheme of orbital interaction. It must be understood that the creation of my idea or proposal and the subsequent applications as described in my article [1] can obviously only be from a theoretical physicist who must not only have a master mind in quantum mechanics but also must have the greatest general attributes or abilities for doing science. They include the first attempt for the unification or "harmony" described! They are prerequisite and also essence for all the development as seen! There must be no any knowledge of chemistry that includes Walsh correlation diagram method and the scheme of orbital interaction that can "lead to" or "induce" what have been

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described as the firsts in my article [1]. There must be also no any essential and decisive role from them that is for the development of my idea or proposal stated. The knowledge of chemistry are simply or at most the confirmation for my idea or proposal stated, that leads to the various applications that include physical nature of chemical bonds. The knowledge of chemistry that include Walsh diagram correlation method and the scheme of orbital interaction cannot apply or be applicable to the creation of my ideal or proposal in any sense, that actually have at most been possibly used or employed for the confirmation only. As has been seen, under the persecution and oppression, I have cited too many papers by others in my article [1], that is obviously not appropriate. Seen from its context, this citation is actually the demonstration of my exceedingly highest quality work that is in contrast to those cited. It is also the invitation of their applause, and has obviously not given any originality or precedence to them. I want to tell that in the most recent version of my article on physical nature of chemical bonds, I have cited only the classical book by Linus Pauling that should be also by courtesy [3].[4] It is obviously not proper to cite the paper by Roald Hoffmann stated here too. In like manner, there must be no any originality and no any precedence in all of my researches or research achievements in the same fields that are from Ronald Hoffmann. It is in any way unlawful for arXiv to allow someone unknown or Roald Hoffmann himself to change the citation of my article [1] as being discussed that must be corrected and punished![5]

It must be therefore known or understood that Roald Hoffmann must not have any major contributions in the basic fields of chemical bonds. First, as has been described, the scheme of orbital interaction is mainly the orbital visualization version of Walsh correlation diagram method, both of which are extremely limited in their practicing as must be known and understood. Also, there is an essential difference between nature and interpretation with

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[4] The first address of physical nature of chemical bond is by Linus Pauling whose quantum mechanics book is one of the classical books in quantum mechanics as known. The second pursue of physics nature of chemical bond is by Klaus Rudenberg who is known as a physicist by training.

[5] It is also illegal for arXiv to modify the dates for a couple of versions of this article, and additionally add the section on dung QM/MM to this article of mine [1] that must be removed! In fact, the date for the second version of this article [1] should be about only one day difference compared to its previous first version by removing the second coauthorship given to Alexander Dalgarno.

nature starting from the power of prediction. Second, as a matter of fact, stating nature or interpretation of chemical bonds with the same or near energies cannot be directly from general quantum mechanical perturbation theory. It has been declared as the consequence of much more general energy scale principle that I have propounded and for which I have a most recent submission as can be seen in the Attachment 2a of my other two complaints with the case #s: 18-cv-02082 or 18-cv-02088. Energy scale principle has included the simple situation of the same or near degenerate energies from general quantum mechanical perturbation theory, and is far beyond it that is for all kinds of quantum interaction among all types of quantum matters in the universe as has been stated or described. Third, as has been mentioned, except conservation of molecular orbital symmetry that R. B. Woodward and Roald Hoffman create, Road Hoffmann must be an ordinary practitioner in the fields of chemical bonds. As has been observed, his understanding of varied chemical bonds has been still within the traditional concepts and domains. His applications of the scheme of orbital interaction that he has advocated in his school have been at most limited to valence or valent bond in chemistry. Probably correspondingly, he has not been able to apply the scheme of orbital interaction for the study of varied chemical bonds and also for the study of so much variety of bonding phenomena in chemistry. It must be also understood that conservation of molecular orbital symmetry for the study of chemical reactivity must obey energy scale principle first that is before the so-called symmetry. It is totally immoral for Roald Hoffmann to be corroding or damaging my understanding and practicing of varied chemical bonds by falsifying his more practicing or involvement in varied chemical bonds and bonding phenomena in his publications as has just been seen or seen most recently. For example, his recent application of the concept of quantum interference for the corresponding explanation of bonding is a strange and sudden occurrence that is a fraud too.[6] As can be thus concluded,

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[6] See his papers cited as: J. Chem. Phys. 141, 224311 (2014) and Proc. Natl. Acad. Sci. USA 113, E 413-419 (2016). It is suspicious that even Yiachung Chang has been invited to be in this fraud known from his paper cited as: Phys. Chem Chem. Phys 17, 6606-6611 (2015), that is also improper too! As must be known or seen, Yiachung Chang has not even been cultured and is very low in his own researches. It is irregular that this kind of the presentation or understanding for his researches is even at his age of retirement that should be only eligible. Besides, from the journal name of this paper, this fraud should be related to Alexander Dalgarno as can be seen from my complaint to him filed recently with the case #:

there have been no major contributions from Ronald Hoffmann in the basic fields of chemical bonds, and all of his contributions in the fields of chemical bonds is not even comparable to my creation of physical nature of chemical bonds. For being a decent and professional chemist, he must apply my quantum interaction and energy scale principle and the resulting physical nature of chemical bonds for his continuing investigation of varied chemical bonds and bonding phenomena in chemistry. It is not wise at all for him to steal, damage, and oppress my idea or proposal as have been stated! In particular, it is totally a criminal conduct that Roald Hoffmann has also stolen the one application of my general quantum mechanical perturbation theory to the solution of energy eigenequation for single-particle states that is also my basis set theory as described!

It must be understood that Roald Hoffmann must have invited me to be a faculty member after receiving my letter to him in September 1998 if he is a respectable Nobel laureate or simply a respectable senior faculty member. This must be totally opposed to his continuously committing thefts as have been observed, that is against the basic norms mandated even for an ordinary teacher. It is unfortunate that Roald Hoffmann has been seen as a representative of nonethics and corruption in scientific community of the United States! His recent lead with Neil Ashcroft in computation beginning around 2010 that is the steal of my researches and my research fields for the study of pressure or temperature effects on electronic structures of solids and others is another extremely barbarous conduct, labeling him as new racist and new colonist! Certainly, there will be another lawsuit against him and Neil Ashcroft too on this concern too.[7] Obviously, the investigation of electronic structures of solids and others and their interplay with pressure or temperature is also the territory of mine and mine only that I have independently created and established since 1989! Here, it is also not wise at all for Roald Hoffmann together with Neil Ashcroft to commit the thefts, making the false publications, and also apply the urine DFT for all their computation, that must be clean![8] He must know my researches and research achievements in quantum

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18-cv-10791, that is the one change of the falsification described there.

[7] He also needs to remove his publications on the pressure effects on the electronic structures of solids, in addition to that of temperature, because it is the subsequent subfield of mine too.

[8] See the Attachment 4 of my other two complaints with case #s: 18-cv-02082 or

statistical mechanics from the year of 1989 too. In addition to the stated invitation for me for a faculty member in the United States, he must have recommended governmental buy for my researches and my research fields as have been known in order for him to do descent and legal researches. It is extremely evil and brutal that the most civilized place as must be observed has seen the most uncivilized matter that is from Roald Hoffmann et al in the United States! He and his cooperators have committed the crime of robbery and murdering, and they are all wild animals and criminals!

To conclude, Roald Hoffmann et al have stolen, damaged, and oppressed my proposal on applying general quantum mechanical perturbation theory for both the qualitative understanding of all the chemical bonds and also the quantitative investigation of all the electronic structures for molecules and solids at various stages, that now is particularly for the address of energy eigenequation for single-particle states that is my basis set theory as has been described in this complaint. International Journal of Quantum Chemistry (IJQC) of John Wiley & Sons has been involved and participated in the steal described by allowing the publication of the paper by Roald Hoffmann and his coauthors and cited as: Int. J. Quant. Chem. 77, 408-420 (2000) as being discussed and also the falsification afterwards by them. National Science Foundation (NSF) has been involved and participated in the steal described by supporting the stealing and falsifying researches shown in the papers by Roald Hoffmann and his coauthors. ArXiv has been involved and participated in the stated steal, damage, and oppression by allowing someone unknown or Roald Hoffmann himself to add the citation, change the dates of different versions of my article [1], and add the section as described. They are all criminals! Please have an attainable investigation of the steal and also a ready technical confirmation of the falsifications described in this complaint, and have all the criminals prosecuted as soon as possible. The corresponding laws or statutes for jurisdiction over this crime, that is steal and falsifications and the resulting damages, are pending for assignment from a judge in the Court.[9] In addition to the attainable investigation of the steal and also the ready technical confirmation of the falsifications as described, I am currently

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18-cv-02088.

[9] I cannot find any of the United States codes other than 18 U.S.C. § 641, § 1001, § 2319 that can be for this jurisdiction.

specifically making the following requests:

(1) The Court must order Roald Hoffmann and his coauthors to rescind or revoke their paper cited as: Int. J. Quant. Chem. 77, 408-420 (2000) as being discussed here immediately and completely.

(2) The Court must order Roald Hoffmann not to steal, damage, and oppress any of my researches, and not to obstruct any of my career development. This includes the stop of his block of all my articles for publication in scientific journals. He cannot be a part or a major figure of the international criminal gang, aiming at stealing my money, robbing my researches, obstructing my career development, and therefore murdering me!

(3) Particularly, the Court must order Roald Hoffmann not to block the publication of my articles [1 – 4], the newest versions of the two of which have now been seen in my other two complaints.

(4) There must be the similar matters for IJQC of John Wiley & Sons. Particularly, it cannot continue to publish those papers that are fraud and steal of my researches.

(5) There must be the similar matters for NSF. Particularly, it cannot continue to financially support those researches that are fraud and steal of my researches.

(6) There must be the similar matters for arXiv. Particularly, it cannot continue to falsify my articles published there and also publish those papers that are fraud and steal of my researches.[10]

Further, I am requesting the Court to order Roald Hoffmann and his coauthors, IJQC of John Wiley & Sons, NSF, and arXiv to compensate all the damages to me as will be described in Relief that is Attachment 4 in this complaint. In the meantime, I want to state that this civic complaint must proceed further or be elevated to the criminal complaint from the Court! There will be more against all the misconducts and crimes from Roald Hoffmann that have been seen or will be disclosed more!

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[10] This complaint applies to all the falsifications to all my articles there by arXiv that must be all removed!

Statement of Claim   05/18/2018   **Liqiang Wei**

References:

[1] L. Wei, "Exploring the Harmony between Theory and Computation – Toward a Unified Electronic Structure Theory", submitted (2017). [*arXiv*: physics/0307156 (2003)]

[2] L. Wei, "Single-Particle Green Function Approach and Correlated Atomic or Molecular Orbital", submitted (2017). [*arXi:* physics/0412174 (2004)]

[3] L. Wei, "On Physical Nature of Chemical Bonds", to be submitted (2020).

[4] L. Wei, "On General Quantum Many-Body Theory", to be submitted (2018). [LOC Registration #: TXu 1-987-576]

Attachment 2　　　　　　　　　　　　　　**05/18/2018**　　　　　　　　　　　　　　**Liqiang Wei**
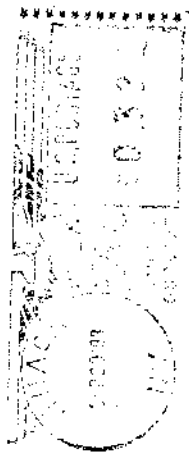
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Generalized Perturbational Molecular Orbital (PMO) Theory*

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ABSTRACT: The useful perturbation expressions for wave functions and energies that are needed in perturbational molecular orbital (PMO) theory are rederived and generalized in two aspects: First, degenerate systems now can be treated in a systematic manner, as in the case of nondegenerate systems. Second, the new expressions can cope with complex wave functions. Two examples of applications to degenerate systems are given to show the qualitative and quantitative utility of the new expressions. © 2000 John Wiley & Sons, Inc. Int J Quant Chem 77: 408–420, 2000

Introduction

The most successful theoretical approach to the electronic structure of molecules has been through the molecular orbital (MO) approximation and its implementation in computational programs at many different levels of sophistication. Propelled by rapidly developing computer technology, MO calculations have become easier, and the systems dealt with accurately have increased in their size.

Qualitative MO theory also has played an essential role in the field 1–3. Mere agreement between numerical calculations and experimental results often does not satisfy chemists, unless an apprehendable rationalization—an explanation couched in words and accessing trends—is given. Qualitative MO theory often shows why the numerical results turn out as they do. It also provides a means for guided speculation about molecular properties that could lead to new experiments and to further detailed quantum mechanical calculations.

Over the years, the perturbational molecular orbital (PMO) method has been an important part of the apparatus of qualitative MO theory 2. To understand the electronic structure of a complicated molecule, it is fruitful to relate it to a simpler one. A difference (between the electronic structure of the complex molecule and its simpler model) may then be thought of as a consequence of a certain perturbation, a distinction in their geometries or constituents. Three different types of perturbation are commonly encountered in electronic structure problems—intermolecular, geometry, and electronegativity perturbations 2. Combined

with a fragment orbital formalism, the PMO method has been very useful in analyzing these problems systematically.

In ordinary perturbation theory, a perturbation is expressed mathematically by a perturbed Hamiltonian in the Schrödinger equation describing the whole system 4,5 . With atomic orbitals as a basis set, these perturbations manifest themselves as changes in Hamiltonian and overlap matrix elements. Therefore, it is natural to employ those matrix elements in deriving the expressions of energies and wave functions of the perturbed system. Such expressions were derived in the work of Imamura 6 , Libit and Hoffmann 7 , and Whangbo et al. 8 .

Imamura first developed a general PMO method that is particularly useful within the extended Hückel method, a simple approximate MO procedure. Here, atomic orbital coefficients were used to express all the perturbation terms for both nondegenerate and degenerate systems. Imamura's formulas for nondegenerate systems were reformulated by Libit and Hoffmann within a fragment orbital formalism. Whangbo showed that the PMO method can be useful even within the Hartree-Fock approximation. The fragment orbital formalism was employed to derive the energies and orbital coefficients for both nondegenerate and degenerate systems. It was shown how the coefficient expressions in terms of fragment and atomic orbitals can be directly related. Whangbo et al.'s work does not contain the expressions for the higher-order perturbation terms of energies and orbital coefficients for the degenerate systems. These are sometimes useful and will be provided here. We also found a few misprints in the published expressions for the nondegenerate systems.

A second contribution of this article is that we generalize the PMO method for complex wave functions, something that has not been done generally earlier. This derivation is vital for the perturbational crystal orbital (PCO) method recently developed in our group 9 . This PCO method allows one to treat and analyze electronic-band structures of extended systems by using crystal orbitals.

Notation and Definitions

In this section, we describe the notation that we are going to use throughout the article. The notation is built upon earlier work of Imamura 6 , Libit and Hoffmann 7 , and Whangbo et al. 8 . At the end of this section, we set up the master equations for various orders of the perturbation theory, which we use later for the derivation of corresponding perturbative expressions for nondegenerate and degenerate cases.

In quantum chemistry, one is concerned with finding the solution for the time-independent Schrödinger equation for a given molecule or a solid:

$$\hat{H}\ \Psi^0\rangle\quad e^0\ \Psi^0\rangle. \tag{1}$$

The PMO theory that we deal with in this article is based on a one-electron approximation to the Schrödinger equation. In this model, the exact Hamiltonian $\hat{H}$ is replaced by $\hat{H}^{eff}$, where an electron interacts only with the average field created by other electrons and nuclei. Consequently, the exact Schrödinger equation (which includes all electrons interacting with each other) is replaced by a series of one-electron equations for electrons $i\ \ 1,\dots,N$:

$$\hat{H}^{eff}\ \Psi_i^0\rangle\quad e_i^0\ \Psi_i^0\rangle. \tag{2}$$

The perturbation theory that we develop is independent of the particular form of the effective one-electron Hamiltonian Eq. (2) . On the other hand, one has to choose a certain one-electron formalism when the perturbation theory results are applied to a specific molecule or a solid. When illustrating applications of the molecular perturbation theory, we use the extended Hückel 10–12 approximation for the effective Hamiltonian. For the sake of notational simplicity, we substitute $\hat{H}^{eff}$ by $\hat{H}$ throughout the remainder of the article.

MOs are usually built up as linear combinations of atomic orbitals (LCAO). The MO $\Psi_i^0\rangle$ can be expended linearly in the atomic orbital basis as

$$\Psi_i^0\rangle\quad \sum_\nu c_{\nu i}^0\ \chi_\nu\rangle, \tag{3}$$

where $\chi_\nu\rangle$ is atomic orbital ν, weighted in sum 3 by the atomic orbital coefficient $c_{\nu i}^0$. We now substitute $\Psi_i^0\rangle$ in Eq. (2) by its expansion from Eq. (3) and premultiply that new equation Eq. (4) by $\langle\chi_\mu$:

$$\hat{H}\left(\sum_\nu c_{\nu i}^0\ \chi_\nu\rangle\right)\quad e_i^0\left(\sum_\nu c_{\nu i}^0\ \chi_\nu\rangle\right), \tag{4}$$

$$\sum_\nu\langle\chi_\mu\ \hat{H}\ \chi_\nu\rangle c_{\nu i}^0\quad e_i^0\left(\sum_\nu c_{\nu i}^0\langle\chi_\mu\ \chi_\nu\rangle\right), \tag{5}$$

$$\sum_\nu\left(H_{\mu\nu}^0\quad e_i^0 S_{\mu\nu}^0\right)c_{\nu i}^0\quad 0, \tag{6}$$

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where $H^0_{\mu\nu} \equiv \langle \chi_\mu \hat{H}^0 \chi_\nu \rangle$ and $S^0_{\mu\nu} \equiv \langle \chi_\mu \chi_\nu \rangle$. Secular Eq. (6) permits one to calculate energies e^0_i and atomic orbital coefficients $c^0_{\nu i}$, if the effective Hamiltonian matrix elements $H^0_{\mu\nu}$ and the atomic orbital overlap matrix elements $S^0_{\mu\nu}$ are known.

In perturbation theory, one assumes that the solution for the original Eq. (6) is explicitly known. Next, Hamiltonian and overlap matrix elements are altered in some well-defined way, which specifies the perturbation. Typical examples include (1) an interaction of two previously noninteracting molecular fragments (an intermolecular perturbation), (2) a geometry change within a molecule (a geometry perturbation), and (3) a substitution of one atom by another (which may be viewed as an electronegativity perturbation). A new secular equation has to be written with altered matrix elements $H_{\mu\nu}$ and $S_{\mu\nu}$:

$$\sum_\nu (H_{\mu\nu} - e_i S_{\mu\nu}) c_{\nu i} = 0. \qquad (7)$$

Note that we have dropped the superscript 0 from all terms in Eq. (7).

Now, we make a connection between the new and old Hamiltonian and overlap matrix elements in the atomic basis. If those changes are relatively small, then

$$H_{\mu\nu} = H^0_{\mu\nu} + \delta H_{\mu\nu}, \qquad (8)$$

$$S_{\mu\nu} = S^0_{\mu\nu} + \delta S_{\mu\nu}. \qquad (9)$$

In any sort of quantitative description, one has to calculate, first, $\delta H_{\mu\nu}$ and $\delta S_{\mu\nu}$ in Eqs. (8) and (9). However, it is often more convenient to express these changes in the MO basis:

$$H_{ij} = H^0_{ij} + \tilde{\Delta}_{ij}, \qquad (10)$$

$$S_{ij} = \delta_{ij} + \tilde{S}_{ij}. \qquad (11)$$

In the last equation, it is assumed that the MO basis set, unlike the atomic orbital basis set, is orthonormal, that is, $S^0_{ij} = \delta_{ij}$. To evaluate Eqs. (10) and (11), an explicit relationship is needed between the matrix elements in the MO basis and those in the atomic orbital basis. This connection may be established in the following way:

$$e^0_i \delta_{ij} = \langle \Psi^0_i H^0 \Psi^0_j \rangle$$
$$= \sum_{\mu,\nu} c^0_{\mu i} \langle \chi_\mu H^0 \chi_\nu \rangle c^0_{\nu j} = \sum_{\mu,\nu} c^0_{\mu i} H^0_{\mu\nu} c^0_{\nu j}, \qquad (12)$$

$$\delta_{ij} = \langle \Psi^0_i \Psi^0_j \rangle = \sum_{\mu,\nu} c^0_{\mu i} \langle \chi_\mu \chi_\nu \rangle c^0_{\nu j} = \sum_{\mu,\nu} c^0_{\mu i} S^0_{\mu\nu} c^0_{\nu j}, \qquad (13)$$

$$\tilde{\Delta}_{ij} = \langle \Psi^0_i \delta H \Psi^0_j \rangle$$
$$= \sum_{\mu,\nu} c^0_{\mu i} \langle \chi_\mu \delta H \chi_\nu \rangle c^0_{\nu j} = \sum_{\mu,\nu} c^0_{\mu i} \delta H_{\mu\nu} c^0_{\nu j}, \qquad (14)$$

$$\tilde{S}_{ij} = \langle \Psi^0_i \Psi^0_j \rangle$$
$$= \sum_{\mu,\nu} c^0_{\mu i} \langle \chi_\mu \chi_\nu \rangle c^0_{\nu j} = \sum_{\mu,\nu} c^0_{\mu i} \delta S_{\mu\nu} c^0_{\nu j}. \qquad (15)$$

In the following derivations, we use mostly the left-hand equalities in Eqs. (12)–(15), keeping in mind that the right-hand double summations are necessary for obtaining numerical answers in any real perturbational calculation (see the Applications section).

If the perturbations Eqs. (10) and (11) are relatively small, then new energies e_i and new wave functions may be expressed as a series expansion, where the superscript n is the order of the perturbation:

$$e_i = e^0_i + e^1_i + e^2_i + \cdots, \qquad (16)$$

$$\Psi_i \rangle = \Psi^0_i \rangle + \Psi^1_i \rangle + \Psi^2_i \rangle + \cdots, \qquad (17)$$

$$\Psi^n_i \rangle = \sum_j t^n_{ji} \Psi^0_j \rangle, \qquad (18)$$

$$\Psi_i \rangle = \sum_j \left(t^0_{ji} \Psi^0_j \rangle + t^1_{ji} \Psi^0_j \rangle + t^2_{ji} \Psi^0_j \rangle + \cdots \right). \qquad (19)$$

The n-th order corrections to the original wave function are obtained as a linear combination of the zeroth-order MOs with the expansion coefficients t^n Eq. (18) . If we are able to calculate the elements of the t matrix and the energy corrections to any order n, and given the convergence of series (16) and (17), then by carrying out the summation of these series we should be able to obtain the exact solution of Eq. (7). However, the first few terms in expansions (16) and (17) are often sufficient for the qualitative (and often quantitative) description of chemical interactions. In this article, we derive the perturbation expansion up to second order both in energies and wave functions.

By substituting the atomic orbital expansion for $\Psi_i \rangle$ Eq. (18) into the left and right sides of Eq. (17), the relationship between the transformation matrix t's and atomic orbital coefficients c's can

be established as follows:

$$\sum_{\nu} c_{\nu i}^{n} \, \chi_{\nu} \rangle \quad \Psi_i^n \rangle \quad \sum_{j} t_{ji}^{n} \Psi_j^0 \rangle \quad \sum_{j,\nu} t_{ji}^{n} c_{\nu j}^{0} \, \chi_{\nu} \rangle, \tag{20}$$

$$c_{\nu i}^{n} \quad \sum_{j} c_{\nu j}^{0} t_{ji}^{n}. \tag{21}$$

We infer from Eq. (21) that the n-th order corrections to the atomic orbital coefficients c^n can be obtained by multiplying from the right the zeroth-order coefficient matrix c^0 by the n-th order transform matrix t^0. This equation enables us to move in perturbative expansions from atomic bases to the molecular bases and vice versa.

At this point, all the tools are at hand for the deducing a master equation which will serve as a starting point for the derivations of both nondegenerate and degenerate corrections to the energies and wave functions. This master equation may be obtained in the following way: First, Eq. (22) for the new (perturbed) system is premultiplied by old wave function $\langle \Psi_j^0$, which leads to Eq. (23). This equation can be rewritten in the atomic basis by the substitution of molecular wave functions by their corresponding atomic expansion Eq. (3) Eq. (24). The new atomic orbital expansion coefficients $c_{\nu i}$ may be replaced by the perturbative expansion Eq. (17) and Eq. (21):

$$\hat{H} \, \Psi_i \rangle \quad e_i \, \Psi_i \rangle, \tag{22}$$

$$\langle \Psi_j^0 \, \hat{H} \, \Psi_i \rangle \quad c_i \langle \Psi_j^0 \, \Psi_i \rangle, \tag{23}$$

$$\sum_{\mu,\nu} c_{\mu j}^{0} H_{\mu\nu} c_{\nu i} \quad e_i \sum_{\mu,\nu} c_{\mu j}^{0} S_{\mu\nu} c_{\nu i}, \tag{24}$$

$$\sum_{k} \sum_{\mu,\nu} \left[(c_{\mu j}^{0} H_{\mu\nu} c_{\nu k}^{0}) t_{ki} \quad e_i (c_{\mu j}^{0} S_{\mu\nu} c_{\nu k}^{0}) t_{ki} \right] \quad 0. \tag{25}$$

Equation (25) contains new Hamiltonian and overlap matrix elements $H_{\mu\nu}$ and $S_{\mu\nu}$ which may be evaluated with the help of Eqs. (8) and (9). Then, the summations over μ and ν can be carried out explicitly, with the help of Eqs. (12)–(14):

$$\sum_{\mu,\nu} \left(c_{\mu j}^{0} H_{\mu\nu} c_{\nu k}^{0} \right) \quad \sum_{\mu,\nu} c_{\mu j}^{0} \left(H_{\mu\nu}^{0} \quad \delta H_{\mu\nu} \right) c_{\nu k}^{0}$$

$$e_j^0 \delta_{jk} \quad \bar{\Delta}_{jk}, \tag{26}$$

$$\sum_{\mu,\nu} \left(c_{\mu j}^{0} S_{\mu\nu} c_{\nu k}^{0} \right) \quad \sum_{\mu,\nu} c_{\mu j}^{0} \left(S_{\mu\nu}^{0} \quad \delta S_{\mu\nu} \right) c_{\nu k}^{0}$$

$$\delta_{jk} \quad \bar{S}_{jk}. \tag{27}$$

Equation (25) now may be rewritten with only one summation over index k:

$$\sum_{k} \left[e_j^0 \delta_{jk} \quad \bar{\Delta}_{jk} \quad e_i \bar{S}_{jk} \quad e_i \delta_{jk} \right] t_{ki} \quad 0. \tag{28}$$

Only energies e_i and wave-function mixing coefficients t_{ki} remain unknown in the last equation. By explicitly performing double summations in the atomic basis Eqs. (26) and (27), we have set up the perturbational problem in the MO basis. By expressing energies e_i and wave-function mixing coefficients t_{ki} through corresponding perturbative expressions Eqs. (16) and (17), the desired master equation of PMO theory is found:

$$\sum_{k} \left[\left(e_j^0 \quad e_i^0 \right) \delta_{jk} \quad \left(\bar{\Delta}_{jk} \quad e_i^0 \bar{S}_{jk} \quad e_i^1 \delta_{jk} \right) \right.$$

$$\left. \left(e_i^2 \delta_{jk} \quad e_i^1 \bar{S}_{jk} \right) \quad \cdots \right] (t_{ki}^0 \quad t_{ki}^1 \quad t_{ki}^2 \quad \cdots)$$

$$0. \tag{29}$$

Here, we assume that H^0 and S^0 in Eqs. (8) and (9) are zeroth-order quantities and, correspondingly, δH and δS are first-order quantities. Then, various terms on the left-hand side of Eq. (29) may be regrouped according to their orders of magnitude. Each of these terms is, in turn, set to zero, which ensures that Eq. (29) is always satisfied:

$$\sum_{k} \left[\left(e_j^0 \quad e_i^0 \right) \delta_{jk} t_{ki}^0 \right] \quad 0, \tag{30}$$

$$\sum_{k} \left[\left(e_j^0 \quad e_i^0 \right) \delta_{jk} t_{ki}^1 \quad \left(\bar{\Delta}_{jk} \quad e_i^0 \bar{S}_{jk} \quad e_i^1 \delta_{jk} \right) t_{ki}^0 \right] \quad 0, \tag{31}$$

$$\sum_{k} \left[\left(e_j^0 \quad e_i^0 \right) \delta_{jk} t_{ki}^2 \quad \left(\bar{\Delta}_{jk} \quad e_i^0 \bar{S}_{jk} \quad e_i^1 \delta_{jk} \right) t_{ki}^1 \right.$$

$$\left. \left(e_i^2 \delta_{jk} \quad e_i^1 \bar{S}_{jk} \right) t_{ki}^0 \right] \quad 0. \tag{32}$$

The MOs which are obtained from Eqs. (30)–(32) are not properly normalized. Normalization conditions have to be applied directly in each order in the perturbation series, which, in turn, determines the diagonal corrections to the wave functions (t_{ii}^n):

$$\langle \Psi_i \, \Psi_i \rangle \quad 1, \tag{33}$$

$$\sum_{k} t_{ki}^{0*} t_{ki}^{0} \quad 1, \tag{34}$$

$$t_{ii}^{1*} \quad t_{ii}^{1} \quad \bar{S}_{ii} \quad 0, \tag{35}$$

$$t_{ii}^{2*} \quad t_{ii}^{2} \quad \sum_{k} \left(t_{ki}^{1*} t_{ki}^{1} \quad t_{ki}^{1*} \bar{S}_{ki} \quad t_{ki}^{1} \bar{S}_{ik} \right) \quad 0. \tag{36}$$

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The wave function Ψ_i expressed in the way above can have an arbitrary phase. A convenient way to fix its phase is just to make t_{ii} real. It follows that t_{ii}^n for any n is a real number as well. As we will see later, when working with complex wave functions, the phases of all other t_{ji}^n's are uniquely determined by these conditions.

For the nondegenerate perturbation theory, Eq. (30) is satisfied with a t^0 which is a unit matrix, that is, the initial wave functions do not have to be mixed in the zeroth-order. The first-order energy corrections are found from Eq. (31), followed by the first-order corrections to wave functions. This procedure is iteratively applied to higher-order terms. In the next section, we derive energy and wave-function correction for a perturbation in a nondegenerate system.

For two degenerate MOs i and j ($e_i = e_j$), the zeroth-order Eq. (30) does not determine the zeroth-order mixing coefficients for the wave functions. It turns out that, unlike the nondegenerate case, the initial wave functions must be properly mixed in zeroth-order ("prepared for the perturbation") before proceeding to higher-order corrections. The following derivation of higher-order corrections is also conceptually different from the corresponding nondegenerate derivations. Following the treatment of the nondegenerate case, we give the corrections to the energies and wave functions up to second-order for a perturbation in a degenerate system.

Nondegenerate Case

When all unperturbed wave functions, Ψ_i^0's, have different energies (i.e., $e_i^0 \neq e_j^0$, if $i \neq j$), Eq. (30) gives $t_{ji}^0 = 0$ whenever $i \neq j$. To satisfy Eq. (34), therefore, t_{ii}^0 should be 1, because this value should be a real number as defined in the previous section. To summarize,

$$t_{ji}^0 = \delta_{ji}. \tag{37}$$

Upon using Eq. (37), Eq. (31) may be simplified to

$$\left(e_j^0 - e_i^0\right)t_{ji}^1 + \left(\tilde{\Delta}_{ji} - e_i^0\tilde{S}_{ji} - e_i^1\delta_{ji}\right) = 0. \tag{38}$$

When $i = j$, the first term in Eq. (38) disappears and, hence, gives rise to the expression for e_i^1:

$$e_i^1 = \tilde{\Delta}_{ii} - e_i^0\tilde{S}_{ii}. \tag{39}$$

When $i \neq j$, Eq. (38) may be rewritten to obtain t_{ji}^1:

$$t_{ji}^1 = \frac{\tilde{\Delta}_{ji} - e_i^0\tilde{S}_{ji}}{e_i^0 - e_j^0}. \tag{40}$$

Note that in Eq. (40) t_{ji}^1 has a fixed phase. This follows from using t_{ji}^0 expressed in Eq. (37), previously defined as a real number.

To obtain t_{ii}^1, we have to go back to one of the normalization condition formulas, which is, in this case, the expression of first order, Eq. (35). Since t_{ii}^1 is a real number, Eq. (35) leads to

$$t_{ii}^1 = -\frac{1}{2}\tilde{S}_{ii}. \tag{41}$$

Proceeding in a similar manner, we obtain the second-order solutions summarized below:

$$e_i^2 = e_i^1\tilde{S}_{ii} - \sum_{k \neq i}\left(\tilde{\Delta}_{ik} - e_i^0\tilde{S}_{ik}\right)t_{ki}^1 \tag{42}$$

$$t_{ji}^2 = -\frac{1}{2}\tilde{S}_{ii}t_{ji}^1 - e_i^1\frac{\tilde{S}_{ji} - t_{ji}^1}{e_i^0 - e_j^0} - \sum_{k \neq i}\frac{\left(\tilde{\Delta}_{jk} - e_i^0\tilde{S}_{jk}\right)t_{ki}^1}{e_i^0 - e_j^0} \tag{43}$$

$$t_{ii}^2 = -\frac{1}{2}\sum_k\left(t_{ki}^{1*}\tilde{S}_{ki} + t_{ki}^1\tilde{S}_{ik} + t_{ki}^{1*}t_{ki}^1\right). \tag{44}$$

Once again, the t_{ji}^2 values have unique phases. In Eq. (44), t_{ii}^2 has to be real, since the overlap matrix is Hermitian (i.e., $\tilde{S}_{ki} = \tilde{S}_{ik}^*$). In other words, Eq. (44) can be reformulated as

$$t_{ii}^2 = -\frac{1}{2}\sum_k\left(t_{ki}^{1*}\tilde{S}_{ik}^* + t_{ki}^1\tilde{S}_{ik} + t_{ki}^{1*}t_{ki}^1\right)$$

$$= -\frac{1}{2}\sum_k\left(2\,Re\left(t_{ki}^1\tilde{S}_{ik}\right) + t_{ki}^{1*}t_{ki}^1\right). \tag{45}$$

By substituting t_{ki} using 40, Eqs. (42) and (43) can be rewritten

$$e_i^2 = e_i^1\tilde{S}_{ii} - \sum_{k \neq i}\frac{\left(\tilde{\Delta}_{ik} - e_i^0\tilde{S}_{ik}\right)\left(\tilde{\Delta}_{ki} - e_i^0\tilde{S}_{ki}\right)}{\left(e_i^0 - e_k^0\right)} \tag{46}$$

$$t_{ji}^2 = \frac{\tilde{S}_{ii}\left(\tilde{\Delta}_{ji} - e_i^0\tilde{S}_{ji}\right) - 2e_i^1\tilde{S}_{ji}}{2\left(e_i^0 - e_j^0\right)} - e_i^1\frac{\left(\tilde{\Delta}_{ji} - e_i^0\tilde{S}_{ji}\right)}{\left(e_i^0 - e_j^0\right)^2}$$

$$- \sum_{k \neq i}\frac{\left(\tilde{\Delta}_{jk} - e_i^0\tilde{S}_{jk}\right)\left(\tilde{\Delta}_{ki} - e_i^0\tilde{S}_{ki}\right)}{\left(e_i^0 - e_j^0\right)\left(e_i^0 - e_k^0\right)}. \tag{47}$$

These expressions have not been given before in their full and correct form.

Degenerate Case

The development of the degenerate perturbation theory is significantly different from the nondegenerate case. It is clear that expressions of the form of Eq. (40) and thereafter have to be somehow modified for degenerate orbitals; otherwise, the denominator would become zero for many terms in the perturbative series. To the best of our knowledge, only expressions for calculating zeroth-order wave functions and first-order corrections to energies for a perturbation in a system with degenerate MOs have been published. We present in this section a consistent and unambiguous procedure for developing degenerate perturbation theory to any perturbative order.

First, a little notational development is in order: We divide the set of original MOs orbitals into two subsets, of degenerate (D) and nondegenerate (N) molecular MOs. We assume for the sake of simplicity that there is only one set of degenerate orbitals, although the extension to multiple sets is straightforward. We denote the subscripts for degenerate MOs by adding a letter D to that subscript and, similarly, for nondegenerate MOs by augmenting the index with N.

ZEROTH-ORDER CORRECTIONS TO WAVE FUNCTIONS AND FIRST-ORDER CORRECTIONS TO ENERGIES

To calculate the zeroth-order correction to wave functions, we start from Eq. (30). If one of the MOs i or j belongs to the nondegenerate set, then $e_j^0 \neq e_i^0$; therefore, $t_{ji}^0 \neq 0$. On the other hand, if both MOs belong to the degenerate set, then $t_{j_D i_D}^0$ remains undefined by this procedure. To calculate zeroth-order correction to degenerate wave functions, we have to use first-order Eq. (31). In this case, since $e_{j_D}^0 \neq e_{i_D}^0$, the following secular equation is set up for the zeroth-order corrections to degenerate wave functions:

$$\sum_k \left(\tilde{\Delta}_{j_D k_D} \quad e_{i_D}^0 \tilde{S}_{j_D k_D} \quad e_{i_D}^1 \delta_{j_D k_D} \right) t_{k_D i_D}^0 \quad 0, \quad (48)$$

$$\begin{vmatrix} \left(\tilde{\Delta}_{11} \quad e_i^0 \tilde{S}_{11} \right) \quad e_{i_D}^1 & \left(\tilde{\Delta}_{i2} \quad e_i^0 \tilde{S}_{12} \right) & \cdots \\ \left(\tilde{\Delta}_{21} \quad e_i^0 \tilde{S}_{21} \right) & \left(\tilde{\Delta}_{22} \quad e_i^0 \tilde{S}_{22} \right) \quad e_{i_D}^1 & \cdots \\ \cdots & \cdots & \cdots \end{vmatrix} \quad 0. \quad (49)$$

First, solution of secular Eq. (49) leads to the first-order energy corrections for the degenerate orbitals. We are making an assumption here that all eigenvalues of secular Eq. (49) are nondegenerate. In this case, a zeroth-order mixing of degenerate MO k_D into MO i_D, $t_{k_D i_D}^0$, can be calculated from Eqs. (48) and (49):

$$\Psi_{i_D}^0 \rangle \quad \sum_k t_{k_D i_D}^0 \Psi_{k_D}^0 \rangle. \quad (50)$$

Instead of the old zeroth-order MOs i_D, we have obtained an equivalent set of new zeroth-order primed MOs i_D'. From the point of view of the original unperturbed problem, the old and new sets of degenerate MOs are completely equivalent. The difference between them arises when a perturbation is introduced—the new zeroth-order wave functions diagonalize not only the original Hamiltonian matrix, but also the first-order perturbation matrix $(\tilde{\Delta}_{j_D k_D} \quad e_{i_D}^1 \delta_{j_D k_D})$. Consequently, possible infinities disappear from Eq. (40).

Here, a notational change has to be introduced for simplifying further analysis. As the new degenerate wave functions $\Psi_{i_D'}^0 \rangle$ are calculated, we drop the prime from their subscripts and use them as if they were the original set of zeroth-order degenerate wave functions. In this new basis set, $t_{k_D i_D}^0$ becomes a unit matrix $\delta_{k_D i_D'}^0$, and, therefore, from Eq. (48) it follows that

$$e_{i_D}^1 \quad \tilde{\Delta}_{i_D i_D} \quad e_{i_D}^0 \tilde{S}_{i_D i_D}. \quad (51)$$

Notice that Eq. (51) looks similar to the analogous Eq. (39) for the nondegenerate perturbation theory. An equivalent expression is found for the first-order corrections to the energy of orbitals belonging to the nondegenerate set in a composite degenerate–nondegenerate system.

FIRST-ORDER CORRECTIONS TO WAVE FUNCTIONS

At this point, we have the correct zeroth-order wave functions and first-order corrections to energies of MOs. Next, the first-order corrections to wave functions have to be computed. If the MO for which this correction is sought belongs to the nondegenerate set of the composite system, then the expression for $t_{j i_N}^1$ is similar to the one from

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Eq. (40):

$$t_{ji_N}^1 = \frac{\tilde{\Delta}_{ji_N} - e_{i_N}^0 \tilde{S}_{ji_N}}{e_{i_N}^0 - e_j^0},\qquad(52)$$

where subscript j indicates both nondegenerate and degenerate MOs.

If MO i belongs to the degenerate set, then the procedure for finding $t_{ji_D}^1$ has to be modified. If j is a nondegenerate MO, then an expression for $t_{j_N i_D}^1$ is found, which is completely equivalent to Eqs. (10) and (52). The derivation is analogous to one for the nondegenerate case (see the previous section) and is omitted here. If j is also a degenerate MO, then the above-mentioned derivation does not work, because $e_{j_D}^0 - e_{i_D}^0 = 0$ in Eq. (38). The second-order Eq. (32) has to be used in order to find the first-order corrections to degenerate MOs $t_{j_D i_D}^1$:

$$\sum_k \Big[\big(e_{j_D}^0 - e_{i_D}^0\big)\delta_{j_D k} t_{k i_D}^2$$
$$+ \big(\tilde{\Delta}_{j_D k} - e_{i_D}^0 \tilde{S}_{j_D k} - e_{i_D}^1 \delta_{j_D k}\big)t_{k i_D}^1$$
$$+ \big(-e_{i_D}^2 \delta_{j_D k} - e_i^1 \tilde{S}_{j_D k}\big)t_{k i_D}^0 \Big] = 0.\qquad(53)$$

The first term in Eq. (53) is identically zero. The second term can be manipulated in the following way:

$$\sum_k \big(\tilde{\Delta}_{j_D k} - e_{i_D}^0 \tilde{S}_{j_D k} - e_{i_D}^1 \delta_{j_D k}\big)t_{k i_D}^1$$
$$= \sum_{k\,D} \big(\tilde{\Delta}_{j_D k_D} - e_{i_D}^0 \tilde{S}_{j_D k_D} - e_{i_D}^1 \delta_{j_D k_D}\big)t_{k_D i_D}^1$$
$$+ \sum_{k\,N} \big(\tilde{\Delta}_{j_D k_N} - e_{i_D}^0 \tilde{S}_{j_D k_N} - e_{i_D}^1 \delta_{j_D k_N}\big)t_{k_N i_D}^1$$
$$= \sum_{k\,D} \big(e_{j_D}^1 \delta_{j_D k_D} - e_{i_D}^1 \delta_{j_D k_D}\big)t_{k_D i_D}^1$$
$$+ \sum_{k\,N} \big(\tilde{\Delta}_{j_D k_N} - e_{i_D}^0 \tilde{S}_{j_D k_N}\big)t_{k_N i_D}^1$$
$$= \big(e_{j_D}^1 - e_{i_D}^1\big)t_{j_D i_D}^1$$
$$+ \sum_{k\,N} \big(\tilde{\Delta}_{j_D k_N} - e_{i_D}^0 \tilde{S}_{j_D k_N}\big)t_{k_N i_D}^1.\qquad(54)$$

When deriving line 3 from line 2 in Eq. (54), we have made use of the fact the the new zeroth-order degenerate wave functions diagonalize the perturbation matrix ($\tilde{\Delta}_{j_D k_D} = e_{i_D}^1 \delta_{j_D k_D}$).

Finally, we have to calculate the third term in Eq. (53):

$$\sum_k \big(-e_{i_D}^2 \delta_{j_D k} - e_{i_D}^1 \tilde{S}_{j_D k}\big)t_{k i_D}^0$$
$$= \sum_k \big(-e_{i_D}^2 \delta_{j_D k} - e_{i_D}^1 \tilde{S}_{j_D k}\big)\delta_{k i_D}^0$$
$$= -e_{i_D}^2 \delta_{j_D i_D} - e_{i_D}^1 \tilde{S}_{j_D i_D} = -e_{i_D}^1 \tilde{S}_{j_D i_D}.\qquad(55)$$

Now, we combine together the three terms in Eq. (53) into a single equation:

$$\big(e_{j_D}^1 - e_{i_D}^1\big)t_{j_D i_D}^1 + \sum_{k\,N} \big(\tilde{\Delta}_{j_D k_N} - e_{i_D}^0 \tilde{S}_{j_D k_N}\big)t_{k_N i_D}^1$$
$$- e_{i_D}^1 \tilde{S}_{j_D i_D} = 0.\qquad(56)$$

The only unknown remaining in Eq. (56) is $t_{j_D i_D}^1$; therefore, it may be expressed in terms of other known quantities as

$$t_{j_D i_D}^1 = \frac{1}{\big(e_{i_D}^1 - e_{j_D}^1\big)}$$
$$\times \Bigg[\sum_{k\,N} \big(\tilde{\Delta}_{j_D k_N} - e_{i_D}^0 \tilde{S}_{j_D k_N}\big)t_{k_N i_D}^1 - e_{i_D}^1 \tilde{S}_{j_D i_D} \Bigg].\qquad(57)$$

Equation (57) can be cast into more explicit form by substituting $t_{k_N i_D}^1$ by its value from Eq. (52):

$$t_{j_D i_D}^1 = \frac{1}{\big(e_{i_D}^1 - e_{j_D}^1\big)}$$
$$\times \Bigg[\sum_{k\,N} \frac{\big(\tilde{\Delta}_{j_D k_N} - e_{i_D}^0 \tilde{S}_{j_D k_N}\big)\big(\tilde{\Delta}_{k_N i_D} - e_{i_D}^0 \tilde{S}_{k_N i_D}\big)}{e_{i_D}^0 - e_{k_N}^0}$$
$$- e_{i_D}^1 \tilde{S}_{j_D i_D} \Bigg].\qquad(58)$$

As seen from Eq. (58), degenerate wave function j_D mixes into another degenerate wave function i_D through two mechanisms: First, it mixes via interaction with a nondegenerate wave function k_N and the subsequent interaction of the latter with i_D. This kind of mixing is reminiscent of the second-order mixing mechanism in the nondegenerate perturbation theory [see Eq. (43)], although here it is a formally first-order process. The small denominator $1/(e_{i_D}^1 - e_{j_D}^1)$ in Eq. (58) makes the expression for $t_{j_D i_D}^1$ first order in magnitude.

Two degenerate wave functions can also mix into each other through the second term in Eq. (58), if there exists a nonzero perturbation ($\tilde{S}_{j_D i_D}$) to the overlap matrix element between those MOs. The renormalization for the degenerate orbitals is done in the same way as for the nondegenerate one. The value of the first-order self-correction to degenerate MO i_D, $t^1_{i_D i_D}$, is calculated according to Eq. (41). In summary, degenerate MOs interact with each other in first order in a way similar to the second-order interactions between nondegenerate MOs.

SECOND-ORDER CORRECTIONS TO WAVE FUNCTIONS AND ENERGIES

Second-order corrections to energies of nondegenerate wave functions of the composite system are computed as prescribed by Eq. (43). To calculate the second-order corrections to energies of degenerate wave functions, we start from Eq. (32), where we set j to i. The first term disappears in Eq. (32) and we are left with the following equation:

$$\sum_k \left[\left(\tilde{\Delta}_{i_D k} \quad e^0_{i_D}\tilde{S}_{i_D k} \quad e^1_{i_D}\delta_{i_D k}\right)t^1_{k i_D}\right.$$
$$\left.\left(\quad e^2_{i_D}\delta_{i_D k} \quad e^1_{i_D}\tilde{S}_{i_D k}\right)t^0_{k i_D}\right] \quad 0. \quad (59)$$

The first and second terms in term in Eq. (59) can be considerably simplified in the same manner as Eqs. (54) and (55):

$$\sum_k \left(\tilde{\Delta}_{i_D k} \quad e^0_{i_D}\tilde{S}_{i_D k} \quad e^1_{i_D}\delta_{i_D k}\right)t^1_{k i_D}$$
$$\sum_{k \ N} \left(\tilde{\Delta}_{j_D k_N} \quad e^0_{i_D}\tilde{S}_{j_D k_N}\right)t^1_{k_N i_D}, \quad (60)$$

$$\sum_k \left(\quad e^2_{i_D}\delta_{i_D k} \quad e^1_{i_D}\tilde{S}_{i_D k}\right)t^0_{k i_D} \quad e^2_{i_D} \quad e^1_{i_D}\tilde{S}_{i_D i_D}. \quad (61)$$

The second-order correction to energies of degenerate wave functions is calculated by substituting Eqs. (60) and (61) into Eq. (59):

$$e^2_{i_D} \quad \sum_{k \ N} \left(\tilde{\Delta}_{i_D k_N} \quad e^0_{i_D}\tilde{S}_{i_D k_N}\right)t^1_{k_N i_D} \quad e^1_{i_D}\tilde{S}_{i_D i_D}. \quad (62)$$

Notice that Eq. (62) is similar to Eq. (42) for the nondegenerate case, except in the former case the summation over k is not carried out for the set of degenerate orbitals. Equation (62) may be rewrit-

ten in more detail by expanding the $t^1_{k_N i_D}$ term:

$$e^2_{i_D} \quad \sum_{k \ N} \frac{\left(\tilde{\Delta}_{i_D k_N} \quad e^0_{i_D}\tilde{S}_{i_D k_N}\right)\left(\tilde{\Delta}_{k_N i_D} \quad e^0_{i_D}\tilde{S}_{k_N i_D}\right)}{e^0_{i_D} \quad e^0_{k_N}}$$
$$e^1_{i_D}\tilde{S}_{i_D i_D}. \quad (63)$$

The second-order correction to *nondegenerate* MOs in a composite system have the same form as that of Eq. (43). If one wants to derive second-order corrections to *degenerate* MOs, then a modified procedure has to be used, similar to one applied in the previous subsection. A third-order analog of Eqs. (30)–(32) becomes a starting point for subsequent computation. Without going into further detail, we provide here only the final expression for calculating the second-order mixing coefficients of nondegenerate MO j_N into degenerate MO i_D and of degenerate MO j_D into degenerate MO i_D. To use these expressions in practical calculations, the previously calculated zeroth-, first-, and second-order corrections to energies and wave functions have to be substituted into Eqs. (64) and (65):

$$t^2_{j_N i_D} \quad \frac{1}{\left(e^0_{i_D} \quad e^0_{j_N}\right)} \sum_{k \ N, \ D} \left(\tilde{\Delta}_{j_N k} \quad e^0_{i_D}\tilde{S}_{j_N k}\right)t^1_{k i_D}$$
$$e^1_{i_D}t^1_{j_N i_D} \quad e^1_{i_D}\tilde{S}_{j_N i_D}, \quad (64)$$

$$t^2_{j_D i_D} \quad \frac{1}{\left(e^1_{i_D} \quad e^1_{j_D}\right)}\left[\sum_{k \ N} \left(\tilde{\Delta}_{j_D k_N} \quad e^0_{i_D}\tilde{S}_{j_D k_N}\right)t^2_{k_N i_D}\right.$$
$$\left. e^1_{i_D} \sum_{k \ N, \ D} \tilde{S}_{j_D k}t^1_{k i_D} \quad e^2_{i_D}t^1_{j_D i_D} \quad e^2_{i_D}\tilde{S}_{j_D i_D}\right]. \quad (65)$$

Up to second-order renormalization of a degenerate wave function leads to second-order self-correction coefficient $t^2_{i_D i_D}$. $t^2_{i_D i_D}$ is calculated as in the nondegenerate theory, that is, using Eq. (44).

Higher-order corrections to wave functions and energies for a system containing degenerate orbitals can be developed in a similar manner: To obtain the n-th-order expression in perturbation theory, first, the corrections to energies are computed, using corrections to wave functions up to the $(n \quad 1)$-th order. Next, the corrections to nondegenerate wave functions are calculated from the n-th-order master equation see Eqs. (30)–(32) . The peculiarity of the degenerate theory is in deriving the n-th-order coefficient of mixing of one degenerate orbital into another from the $(n \quad 1)$-th-order master equation. Diagonal self-correction terms are calculated at the very end, in a similar manner or both nondegenerate and degenerate orbitals.

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Intermolecular Perturbation: Homonuclear Diatomic Molecules

Perhaps one of the simplest examples showing the utility of the degenerate perturbation method is that of homonuclear diatomic molecules, for example, N_2. Within a PMO approach, the MOs of a diatomic molecule can be constructed from atomic orbitals of each atom, the (large) perturbation is the interatomic interaction. Defining the z-axis as the internuclear axis, the basis orbitals naturally separate into $\sigma(s, p_z)$ and $\pi(p_x, p_y)$ types 2 . Here, let us consider just the more interesting σ-type interaction, in which both s and p orbitals participate in MO formation, and, thus, $s–p$ mixing occurs. To proceed, we first obtain the correct zeroth-order wave functions in each degenerate set of s and p orbitals and next consider higher-order perturbation terms for wave-function correction. The higher-order perturbational terms will describe interactions between the zeroth-order wave functions of different types of orbitals (i.e., $s–p$) as well as of the same types of orbitals (i.e., $s–s$ and $p–p$). Since the essential qualitative aspects of these interactions are contained in first-order terms, we limit our discussion in this section to those.

Let us imagine two interacting atoms, 1 and 2, each having two orbitals, χ_s and χ_p (Fig. 1). The same types of orbitals ($s–s$ or $p–p$) are degenerate in energy. When the atoms interact, changes will occur only in off-diagonal (Hamiltonian and overlap) matrix elements describing the interactions
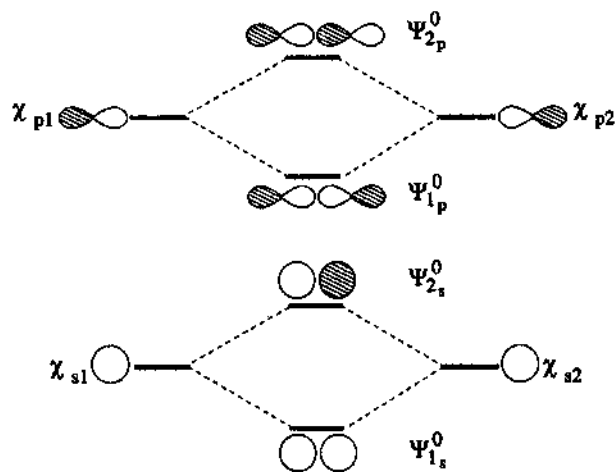
between the atoms. We express those changes by δH_{ss} and δS_{ss}, δH_{pp} and δS_{pp}, and δH_{sp} and δS_{sp} for interactions between two s's, two p's, and one s and one p orbital, respectively. In Figure 1, we arrange the atomic orbitals so that all overlap terms are positive, and, thus, Hamiltonian terms should be all negative. To consider the zeroth-order corrections to the s orbitals, we set up the following secular equation using Eq. (49):

$$\begin{vmatrix} e_{i_s}^1 & (\delta H_{ss} \quad e_s^0\,\delta S_{ss}) \\ (\delta H_{ss} \quad e_s^0\,\delta S_{ss}) & e_{i_s}^1 \end{vmatrix} \quad 0. \quad (66)$$

From Eq. (66), we obtain the first-order energy corrections:

$$e_{1_s}^1 \quad \delta H_{ss} \quad e_s^0\,\delta S_{ss} \quad 0, \quad (67)$$

$$e_{2_s}^1 \quad (\delta H_{ss} \quad e_s^0\,\delta S_{ss}) > 0. \quad (68)$$

The correct zeroth-order wave functions corresponding to $e_{1_s}^1$ and $e_{2_s}^1$ result from substituting those terms in Eq. (66). After normalization using Eq. (34), we get

$$\Psi_{1_s}^0 \quad \frac{1}{\sqrt{2}}(\chi_{s1} \quad \chi_{s2}), \quad (69)$$

$$\Psi_{2_s}^0 \quad \frac{1}{\sqrt{2}}(\chi_{s1} \quad \chi_{s2}). \quad (70)$$

The correct zeroth-order wave functions are drawn schematically in Figure 1. It can be seen that $\Psi_{1_s}^0$ and $\Psi_{2_s}^0$ are orthogonal to each other, the former being symmetric (bonding) and the latter being antisymmetric (antibonding) with respect to a mirror plane at the center perpendicular to the interatomic axis.

Exactly the same procedure is followed to obtain the correct zeroth-order wave functions for p orbitals and their corresponding first-order energy-correction terms. To summarize:

$$e_{1_p}^1 \quad \delta H_{pp} \quad e_p^0\,\delta S_{pp} \quad 0, \quad (71)$$

$$e_{2_p}^1 \quad \left(\delta H_{pp} \quad e_p^0\,\delta S_{pp}\right) > 0, \quad (72)$$

$$\Psi_{1_p}^0 \quad \frac{1}{\sqrt{2}}(\chi_{p1} \quad \chi_{p2}), \quad (73)$$

$$\Psi_{2_p}^0 \quad \frac{1}{\sqrt{2}}(\chi_{p1} \quad \chi_{p2}). \quad (74)$$

FIGURE 1. Correct zeroth-order σ MOs in N_2.

The symmetry properties of the correct zeroth-order wave functions from p orbitals, $\Psi_{1_p}^0$ and $\Psi_{2_p}^0$, are exactly the same as those from s orbitals (Fig. 1). All this is pretty much as one would expect in a qualitative treatment of diatomic formation.

Now, we consider the first-order contribution to each zeroth-order wave function and the corresponding (second-order) energy correction. For this purpose, all matrix elements are calculated by putting Eqs. (69), (70), (73), and (74) into Eq. (15):

$$\tilde{S}_{1,1,} \qquad \tilde{S}_{2,2,} \qquad \delta S_{ss}, \qquad (75)$$

$$\tilde{\Delta}_{1,1,} \qquad \tilde{\Delta}_{2,2,} \qquad \delta H_{ss}, \qquad (76)$$

$$\tilde{S}_{1_p 1_p} \qquad \tilde{S}_{2_p 2_p} \qquad \delta S_{pp}, \qquad (77)$$

$$\tilde{\Delta}_{1_p 1_p} \qquad \tilde{\Delta}_{2_p 2_p} \qquad \delta H_{pp}, \qquad (78)$$

$$\tilde{S}_{1,1_p} \qquad \tilde{S}_{2,2_p} \qquad \delta S_{sp}, \qquad (79)$$

$$\tilde{\Delta}_{1,1_p} \qquad \tilde{\Delta}_{2,2_p} \qquad \delta H_{sp}. \qquad (80)$$

Due to the symmetry properties of the zeroth-order wave functions, all the other terms are zero. One immediate consequence of this will be that there is no contribution to each wave function from its paired zeroth-order wave function. This can be seen by examining Eq. (58), where all matrix elements are zero in this particular case.

The self-contribution terms are obtained from Eqs. (75), (77), and (41):

$$t_{1,1,}^1 \qquad \frac{1}{2}\delta S_{ss}, \qquad (81)$$

$$t_{2,2,}^1 \qquad \frac{1}{2}\delta S_{ss}, \qquad (82)$$

$$t_{1_p 1_p}^1 \qquad \frac{1}{2}\delta S_{pp}, \qquad (83)$$

$$t_{2_p 2_p}^1 \qquad \frac{1}{2}\delta S_{pp}. \qquad (84)$$

The negative signs in Eqs. (81) and (83) means that the self-contribution terms actually reduce the size of the coefficients of the orbitals in $\Psi_{1,}^0$ and $\Psi_{1_p}^0$. The opposite holds for $\Psi_{2,}^0$ and $\Psi_{2_p}^0$.

Now, we consider the first-order contributions to the wave functions. These come from the interaction between $(\Psi_{1,}^0, \Psi_{2,}^0)$ and $(\Psi_{1_p}^0, \Psi_{2_p}^0)$, that is, between two sets of the degenerate pairs. By substituting Eqs. (79) and (80) into Eq. (52), the first-

order coefficients are calculated as

$$t_{1_p 1,}^1 \qquad t_{2_p 2,}^1 \qquad \frac{\delta H_{sp} \quad e_s^0\, \delta S_{sp}}{e_s^0 \quad e_p^0}, \qquad (85)$$

$$t_{1,1_p}^1 \qquad t_{2,2_p}^1 \qquad \frac{\delta H_{sp} \quad e_p^0\, \delta S_{sp}}{e_p^0 \quad e_s^0}. \qquad (86)$$

Since $e_s^0 \quad e_p^0$, $t_{1,1,}^1$ and $t_{2,2,}^1$ are positive, while the opposite sign follows for $t_{1,1_p}^1$ and $t_{2_p 2,}^1$.

Figure 2 shows the perturbed wave functions, whose shapes were drastically changed due to $s-p$ mixing through the first-order orbital corrections. The bonding and antibonding characters of $\Psi_{1,}$ and Ψ_{2_p}, respectively, are enhanced by $s-p$ mixing. However, the two MOs in the middle, $\Psi_{2,}$ and Ψ_{1_p}, became approximately nonbonding. It should be noted that these are schematic drawings, not contour diagrams, of the MOs.

As mentioned earlier, the first-order corrections to wave functions are reflected in the second-order corrections in energies. Substitution of all perturbation terms obtained above into Eq. (62) yields the following:

$$e_{1s}^2 \qquad e_{2s}^2$$

$$\frac{\left(\delta H_{sp} \quad e_s^0\, \delta S_{sp}\right)^2}{e_s^0 \quad e_p^0} \qquad \left(\delta H_{ss} \quad e_s^0\, \delta S_{ss}\right)\delta S_{ss}, \qquad (87)$$

$$e_{1p}^2 \qquad e_{2p}^2$$

$$\frac{\left(\delta H_{sp} \quad e_s^0\, \delta S_{sp}\right)^2}{e_s^0 \quad e_p^0}$$

$$\left(\delta H_{pp} \quad e_p^0\, \delta S_{pp}\right)\delta S_{pp}. \qquad (88)$$

In all the second-order energy expressions above, the second terms are from the self-contributions and they are all positive. Therefore, the first-order self-contributions in wave functions destabilize the original zeroth-order wave functions. This is consistent with the fact that the explicit inclusion of overlap actually raises the energies of bonding and antibonding MOs 10–12 . Meanwhile, the first terms in Eqs. (87) and (88) are negative and positive, respectively. This means that $s-p$ mixing through first-order perturbation in wave functions stabilizes the low-lying s orbitals and destabilizes the high-lying p orbitals (Fig. 2).
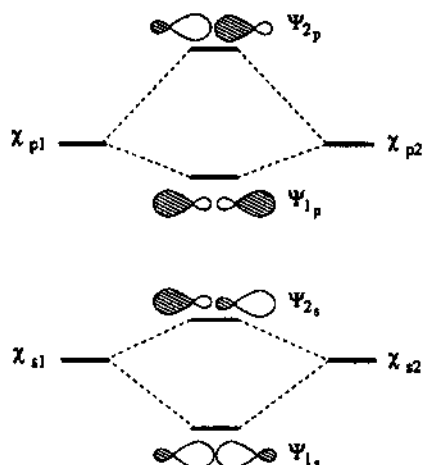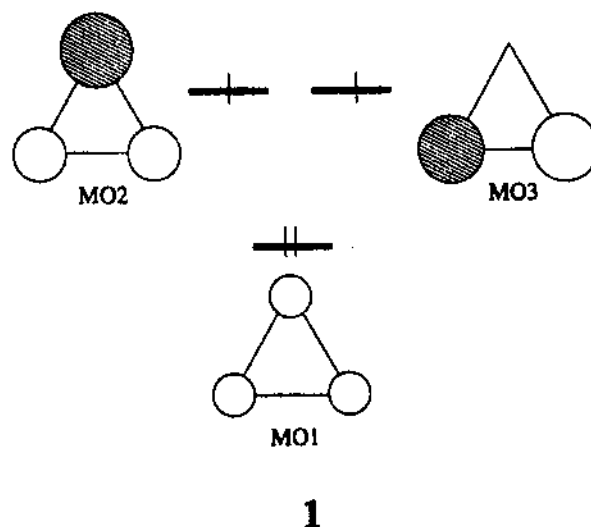
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FIGURE 2. The σ MOs in N_2, with mixing through first order included.

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Geometry Perturbation: A Sliding Distortion of an H₃ Triangle

In this section, we demonstrate that PMO theory is not only a tool for qualitative analysis but may provide quantitative results if needed. Of course, we do not expect perturbation theory to perform better than the underlying theory which it attempts to model (in this case the extended Hückel model).

The MOs of a hypothetical H_3 molecule are depicted below (see **1**). In this molecule, there are two degenerate orbitals, MO2 and MO3, filled with two unpaired electrons. One would expect a Jahn–Teller-type distortion to occur. The distortion that we chose to consider (see **2**) is not a normal mode of the H_3 molecule but a simple horizontal sliding motion of the H3 atom. Other distortions of the H_3 molecule may be analyzed in a similar manner.

The sliding motion of the H3 atom produces two perturbations in the atomic basis set. As a result of H3—H1 bond elongation, its corresponding overlap integral diminishes, along with the corresponding Hamiltonian matrix. The H3—H2 bond gets shorter, which induces opposite changes in the overlap and Hamiltnoian matrix elements.

After calculating the changes in the overlap and Hamiltonian matrix elements in the atomic basis, a transformation is carried out to the molecular basis according to Eqs. (14) and (15). It turns out that the original degenerate orbitals MO2 and MO3 are not

the correct zeroth-order wave functions for this perturbation. To find those, a two-by-two secular equation is set up, as suggested by Eq. (49). Calculated correct zeroth-order degenerate MOs are indicated in Table I. Since MO1 is nondegenerate, it has the correct zeroth-order form from the beginning.

As may be inferred from Table I, just getting the correct zeroth-order degenerate orbitals MO2 and MO3 captures the largest part of the wave-function change during the sliding distortion. Quantitative agreement with the exact solution is obtained when first- and second-order corrections are computed using the formalism developed in this article. For instance, there is a *first-order* mixing of degenerate MO3 into degenerate MO2 through nondegenerate MO1. When corrections up to second-order are considered, the atomic orbital coefficients of the MOs computed from perturbation theory agree to two significant figures with the full
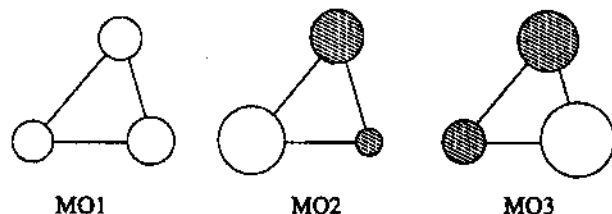

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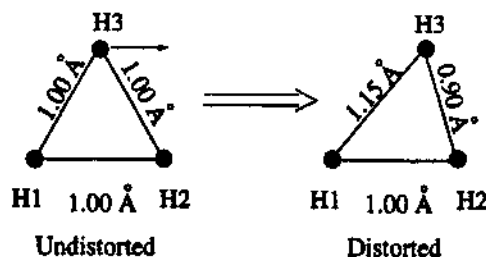
GENERALIZED PMO THEORY

TABLE I
A sliding distortion of an H_3 perfect triangle as described in the text; the entries give the indicated AO coefficients in the perturbative expansions for (a) MO1, (b) MO2, and (c) MO3.

	AO1	AO2	AO3
(a) MO1			
$\Psi_1^0\rangle$ (initial)	0.4148	0.4148	0.4148
$\Psi_1^0\rangle$ (new)	0.4148	0.4148	0.4148
$\Psi_1^0\rangle + \Psi_1^1\rangle$	0.3963	0.4384	0.4143
$\Psi_1^0\rangle + \Psi_1^1\rangle + \Psi_1^2\rangle$	0.3960	0.4361	0.4150
$\Psi_1\rangle$ computed	0.3948	0.4372	0.4150
(b) MO2			
$\Psi_2^0\rangle$ (initial)	0.5601	0.5601	1.1203
$\Psi_2^0\rangle$ (new)	1.0688	0.2439	0.8250
$\Psi_2^0\rangle + \Psi_2^1\rangle$	0.9963	0.1954	0.7406
$\Psi_2^0\rangle + \Psi_2^1\rangle + \Psi_2^2\rangle$	1.0080	0.1987	0.7501
$\Psi_2\rangle$ computed	1.0065	0.1979	0.7489
(c) MO3			
$\Psi_3^0\rangle$ (initial)	0.9702	0.9702	0.0000
$\Psi_3^0\rangle$ (new)	0.3356	1.0934	0.7579
$\Psi_3^0\rangle + \Psi_3^1\rangle$	0.3932	1.1469	0.8320
$\Psi_3^0\rangle + \Psi_3^1\rangle + \Psi_3^2\rangle$	0.3972	1.1554	0.8391
$\Psi_3\rangle$ computed	0.3977	1.1567	0.8403

TABLE II
Distortion of a H_3 perfect triangle as described in the text; perturbative expansion for energies.

Energies (eV)	MO1	MO2	MO3
e^0	18.5357	4.5988	4.5988
$e^0 + e^1$	18.4980	7.8411	1.8629
$e^0 + e^1 + e^2$	18.5044	7.2605	1.4189
e computed	18.5040	7.3469	1.3366

exact extended Hückel calculations. MOs for the distorted molecule are drawn in **3**. It is remarkable that even for such large changes in the shapes of MOs perturbation theory provides quantitative results.

The energies of the MOs were calculate according to Eqs. (39), (42), (51), (62), and (63). The total energy of the H_3 molecule is lowered by 5.43 eV during the sliding distortion, that is, the distortion is stabilizing. The largest part of this energy is contributed by the first-order energy correction to MO2, which actually overestimates the stabilization by 1.0 eV (for two electrons). The second-order correction to the energy of MO2 is essential for

MO1   MO2   MO3

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producing reasonable agreement with this MO exact energy (see Table II).

Finally, we note that the zeroth-order mixing of the degenerate orbitals MO2 and MO3 predetermines the shapes of these MOs. Consider MO2, for example. The H3 orbital in the undistorted molecule has equal antibonding interactions with orbitals H1 and H2 (see **1**). In the correct zeroth-order MO2, however, the H3—H1 bond remains antibonding while the H3—H2 bond becomes bonding (see **3**). When the distortion occurs, the elongation of the H3—H1 bond leads to a weakening of the H3—H1 antibonding interactions. Conversely, the shortening of the H3—H2 bond leads to strengthening of H3—H2 bonding interactions. Therefore, the correct zeroth-order MO2 is set up for the maximum stabilization during the distortion, as is indeed observed. On the contrary, the nodal properties of correct zeroth-order MO3 (**3**) anticipate maximum destabilization during the distortion: H3—H1 bonding interactions are diminished and H3—H2 antibonding interactions enhanced.

Conclusions

Prior to this work, the apparatus of PMO theory for degenerate systems was not fully developed. In particular, we were not able to find in the literature expressions for evaluating the first- and higher-order corrections to wave functions as well as the second- and higher-order corrections to energies of degenerate MOs. It was also not clear how to incorporate degenerate perturbation theory into the more general framework of nondegenerate perturbation theory.

In the first part of this article, we set up the master equations for deriving perturbative expressions up to the second order. If complex wave

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functions are used, as, for instance, one must do for crystal orbitals in the solid state, we suggested that all diagonal corrections to MOs be kept real. In that case, no ambiguity remains in determining the phases of corrections to wave functions.

We rederived the familiar perturbation theory for nondegenerate systems and corrected a small number of misprints found in the literature expressions. For the degenerate systems, we developed a systematic way of determining higher-order corrections to energies and wave functions. By the way that we constructed the theory, the degenerate system is naturally incorporated into a larger nondegenerate–degenerate composite system. One of the peculiarities of degenerate perturbation theory is that the first-order corrections to wave functions look similar to second-order corrections in the nondegenerate case.

Finally, we tested the perturbation theory formalism developed on two cases: N_2 molecule formation out of two N atoms (an intermolecular perturbation) and a sliding distortion of an H_3 triangle (a geometry perturbation). We demonstrated that degenerate perturbation theory may be applied both qualitatively as well as in quantitative calculations.

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Attachment 3   **05/18/2018**   **Liqiang Wei**

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Exploring the Harmony between Theory and Computation - Toward a unified electronic structure theory

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Abstract

The physical aspect of a general perturbation theory is explored. Its role as a physical principle for understanding the interaction among the matters with different levels of hierarchy is appreciated. It is shown that the general perturbation theory can not only be used for understanding the various electronic phenomena including the nature of chemical bonds but also serve as a unified theme for constructing general electronic structure theories and calculation schemes.

Perturbation theory is regarded as one of the two major approaches for approximately solving quantum many-body problems. However, its deeper physical aspect is far more than it is currently being used just as a mathematical tool for solving the complicated issues. All the fundamental laws in physics are variational in nature, including the Schrödinger equation in

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quantum mechanics. Nevertheless, the perturbation theory provides a principle that governs how the matters with different levels of hierarchy interact. In fact, a general perturbation theory itself contains two ingredients. On one hand, the degenerate or near-degenerate situation is *not* a perturbation at all but actually constitutes a strong physical interaction. On the other hand, the non-degenerate case is a real perturbation in the common sense. We believe that, it is this equal or near energy physical mixing that governs the interaction among the matters with different levels of hierarchy. Of course, it is also the physical principle based on which a unified chemical bond theory can be built.

Electrons are quantum mechanical particles which possess wave-particle duality. The binding process of the electrons associated with some atoms, or equivalently, the interaction of atomic orbitals for the formation of a molecule, can be regarded as a wave interference phenomenon. The interaction of *intra*-atomic orbitals with the same energy or near energies is the Pauling's hybridization process, which determines the direction of chemical bonds, while the interaction of *inter*-atomic orbitals with the same energy or near energies determines the actual formation of chemical bonds. These are the nature of chemical bonds [1,2]. The immediate benefit for recognizing this near energy principle in determining the formation of chemical bonds is that it gives a better understanding of many previously developed very important structure concepts such as multi-center chemical bonds, multiple chemical bonds, resonance structure, Walsh diagrams, and avoided crossing, and therefore incorporate them into one *qualiatative* theoretical framework [1,3-5].

More important in realizing this fundamental physics for understanding how the matters interact is that it also provides a physical foundation for *quantitatively* investigating the electronic structure of molecules, including large systems such as molecular materials and biomolecules. We are going to have a harmony between theory and computation.

Energy scale principle in Rayleigh – Ritz variatioanl approach

Rayleigh-Ritz variational method is most commonly used for solving eigenvalue problem in quantum mechanics. Its relation to the general perturbation theory, including the degenerate situation, has also been worked out mathematically during the 1960's [6]. However, the physical implication of this relation, especially its role as a guidance in constructing the electronic structure calculation schemes has not been explored and appreciated yet. First of all, as long as the reference Hamiltonian which produces the basis functions is made as close as possible to the full Hamiltonian, then the dimension for the Rayleigh-Ritz variational expansion will be made as small as possible. Secondly, if the basis functions have the closest energies of the reference Hamiltonian, then they will have the strongest mixing and make the greatest contribution to the combined state, while the others with larger energy differences will have smaller or even negligible contributions. These are the situations we qualitatively discussed above for the general perturbation theory. We term this as the energy scale principle in Rayleigh-Ritz variational approach.

(a) *Molecular fragmentation and basis set construction*

The basis set approach is a most popular and natural way for solving the single particle equation such as Hartree-Fock equation. Physically, it reflects

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a composite relation between the molecule and its constituent atoms. To have an overall accurate electronic structure calculation, the first necessary step is to get the reliable and converged molecular orbitals [7].

However, since the current basis functions like most commonly used contracted Gaussians are primarily a reflection of electrons in single atoms in the molecule, it leaves the perturbed part of the molecular Fock operator very large. That is why the polarization functions, including some expanded ones such as the correlation consistent basis sets, have to be introduced to get good computation results [8]. Nevertheless, the $O(N^4)$ scaling, where N is the number of basis functions, has become a major bottleneck in quantum chemistry calculation, especially for the large systems.

To overcome this difficulty, the energy-scale principle described above can come for a help. If we construct the basis functions which are the reflection of molecular fragments so that the corresponding reference Hamiltonian is as close as possible to the whole molecular Fock operator, then the dimension of basis set expansion can be made as small as possible. This is going to be a challenge work but will be mathematical in nature. The basis set superposition effects (BSSE) is an example [9].

Similar situation occurs in the quantum molecular scattering calculation, where the channels are used as the basis functions for solving the Schrödinger equation, or its integral form, Lippmann-Schwinger equation with proper boundary conditions. Since there are often very large differences between the channels and the scattering waves for the whole reactive system in the interaction regions, the dimension for their expansion is particularly large, which causes the quantum scattering calculation prohibitively expansive for

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all but the smallest systems. The ideas suggested here can obviously be utilized for remedying this deficiency.

(b) *General multi − reference electronic structure theory*

To get final accurate solution to the Schrödinger equation for the many-electron systems with a non-separable two-body Coulomb interaction, it is most likely that we have to go beyond the single particle description [10-13]. Mathematically, the full configuration interaction (FCI) gives exact answers [14]. However, it is computationally prohibitive and possibly will never been strictly realized. The energy scale principle described above can also be applied in this *configuration* level. A general electronic structure theory should be multi-configuration or multi-reference in nature [15-20]. First, there exists a strong configuration mixing, for example, at transition states, for excited states, and for multiple chemical bonds. The concept of exciton introduced in solid state physics also belongs to this case [21]. Second, the degenerate configurations are often the case for the stable open-shell systems. Third, if we want to treat the ground state and the excited states simultaneously, we have to include the corresponding reference states in the same model space. Finally, the separation of correlation into the static and dynamic parts, which corresponds to the near degenerate and the perturbed situations, really has chemical structure signature. Therefore, among all the correlation approaches developed so far for electronic structure, the MCSCF type with perturbation or coupled-cluster expansion correction should be the most appropriate and general one and works in the right direction. To solve the remaining issues such as proper selection of configurations for the model space, the efficient treatment of dynamic correlation, and the avoidance of

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intruder states, we not only need a mastery of current quantum many-body theory but also might need its further development.

The importance and necessity of separation of correlation into a static part and a dynamic part is also indicated in the DFT calculation for the highly charged ions [22] and in its treatment of transition states of reactions [23]. This calls for an extension of current DFT to incorporate the differentiation of static and dynamic correlation effects into its theoretical framework [24,25].

(c) *General pseudopotential theory*

The concepts of pseudopotentials, effective core potentials (ECP), or model potentials (MP) are those of the most significant developments in the fields of electronic structure for molecular and solid state systems. It treats valence electrons only, leaving the core electrons and nucleus as a whole charge entity and therefore reducing the number of electrons as well as the corresponding overall size of the basis set being used for the computation. It is important when we study the electronic structure for large molecules or inorganic molecules containing heavy elements [26]. A most commonly used pseudopotential for solid state calculation is the so-called norm conserving pseudopotential [27]. In addition to having the same valence state energies, its pseudo valence state wavefunctions are also equivalent to the valence state wavefunctions obtained from the full electron calculations outside a cutoff radius. The pseudopotentials constructed in this manner share the same scattering properties as those of the full potentials over the energy range of the valence states. The practical implementation of various pseudopotentials has also demonstrated the importance of choosing a correct size

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of the core or range of the valence electrons for the accurate pseudopotential computation in order that the core-valence correlations or core polarization can be neglected. Obviously, the physics behind this valence and core state separation is the energy scale principle we described above applied in the level of *atomic orbitals*. After realizing this principle, however, we might establish a more general pseudopotential theory. We are planning to reformulate the pseudopotential approach in the framework of perturbation theory so that most flexible and accurate ECPs can be developed. They can be used in different chemical environments and work for both ground and excited state problems. The final goal is to make the effective core potentials to be a routine rather than an approximation for calculating electronic structure for large molecules, inorganic molecules containing heavy elements, and solid state systems.

(d)*Molecular fragmentation and combined QM/MM approach for electronic structure of large molecules*

Combined QM/MM approach has become very popular in recent years in the study of, for example, the chemical reactions in solutions and in enzymes [28,29]. The basic consideration is that treating a full collection of electrons for the whole system explicitly is not only unrealistic but also unnecessary. In the first place, the electronic charge redistribution induced by a chemical reaction is very often limited to a small region due to the length scale issues such as finite range of interaction or natural charge distribution. Second, the quantum exchange effect for the electrons is finite range, and there is no exchange interaction among the electrons with long distance. This permits a partition of the whole system into an active part

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and an inactive part without any charge redistribution. The former has to be described quantum mechanically since it possibly involves bond breaking and making, while the latter can be described by molecular mechanics because it merely serves as a classical electrostatic environment for the active site. This combined QM/MM description has shown remarkable successes in studying the electronic structure and reactivity of large molecules in recent years. However, challenges remain. One of the major obstacles for the applications is in the proper treatment of boundary region where the cut has to be for a covalent bond. Currently, there are two approaches to this problem. The one introducing link atoms along the boundary is severely limited and cannot be applied to treat a large variety of different chemical systems. In addition, it artificially brings additional forces into the system and therefore complicates the problem. The other kind like local self-consistent field methods seems reasonable but it is still more empirical. In order to utilize this kind of combined QM/MM methods for investigating the electronic structure and molecular dynamics in a larger domain of fields, we need to develop a more generic ab initio approach. We believe that the energy scale principle discussed above can play a key role here. It is not only the principle according to which the atomic orbitals including valence ones interact along the boundary but also the principle based on which a systematic approach for constructing the correct charge distribution or the force fields along the boundary can be established. This is also the key for a more sophisticated or finer treatment of quantum region including its electron correlation.

In summary, the energy scale principle for the hierarchy of interacting matters is identified. It not only can be utilized as a general principle for

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understanding how the matters interact at different levels but also can serve as the foundation based on which the accurate electronic structure calculation schemes for even large molecular systems can be constructed. It can also be employed to build *a general theory for the intermolecular forces* so that the important issues such as the interplay between chemical bondings and intermolecular forces can be investigated [30].

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Attachment 4   **05/18/2018**   **Liqiang Wei**

Relief

As has been described in the last paragraph of my Statement of Claim, I have made the requests for the orders from the Court that must be enforced immediately. This is to protect and promote my personal properties that are quantum interaction and energy scale principle and their applications, that especially include my creation of physical nature of chemical bonds and my creation of general electronic structure theories at various stages for molecules and solids here. All the following researches including all the other applications that belong to my territory too cannot be stolen, damaged, and oppressed in any way. If someone wants to carry out the researches of the applications that are on computation, they must cite my articles and also do the business with me.

Because of the steal and falsifications described and the resulting injures that include the damage of my personal properties, destruction of my personal career, and ruin of my personal business, I also want the Court to order Roald Hoffmann, Dong-Kyun Seo, and Garegin A. Papoian; IJQC; NSF; and arXiv to compensate me for all the money. Currently, for only the damage of the corresponding salary for my developments that have been stolen from the paper by Roald Hoffmann, Dong-Kyun Seo, and Garegin Papoian cited as: Int. J. Quant. Chem. 77, 408-420 (2000) as described, I am requesting the compensation from Roald Hoffmann, Dong-Kyun Seo, Garegin A. Papoian; IJQC; and NSF in the total amount of USD 605 million that is before my retirement; and for only the damage of the corresponding partial salary for my developments demonstrated in my article [1] by arXiv as described, I am also requesting the compensation from arXiv in the total amount of USD 370 million that is also before my retirement. This is in the total amount of USD 975 million. All the other compensations including the loss of the business income will be left for the future calculations and compensations.

As must be really understood, the steal and falsifications as has been described has brought a tremendous and inestimable hurts and injuries to me for both of my scientific career and also my personal life and health. It has been seen as robbing and murdering me! Right now, I am living in extreme poorness, and have lost my foods, medications, and residency from these robbing and murdering me! There must be an injunctive relief and

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emergent rescue of me and my life!